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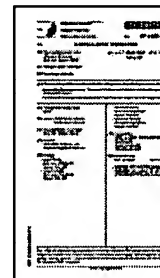
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- 🔍 Title: **EP0626356B1: Ceramic composition, thermistor element, and process for producing a ceramic body**[\[German\]](#)[\[French\]](#)
- 🔍 Derwent Title: Ceramic compsns. suitable for thermistor elements - having broad operating range, resistance to oxidising and reducing atmos. and superior stability at high temps. [\[Derwent Record\]](#)
- 🔍 Country: **EP** European Patent Office (EPO)
- 🔍 Kind: **B1** Patent (See also: [EP0626356A1](#))
- 🔍 Inventor: **Iwaya, Masaki NGK Spark Plug Co Ltd;**
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- 🔍 Priority Number: **1993-05-24 JP1993000144294**
1993-12-22 JP1993000346653
- 🔍 Abstract: [\[From equivalent EP0626356A1\]](#) Described is a ceramic composition of the formula (M1_{1-x}N1_x)(P_y¹-y-zN_y²Al_z)O₃ where M1 is one or more selected from the group 3A elements of the Periodic Table excluding La, N1 is one or more selected from the group 2A elements of the Periodic Table, P_y¹ is one or more selected from the elements of the groups 4A, 5A, 6A, 7A and 8 of the Periodic Table whose oxides exhibit p-type characteristics, and N_y² is one or more selected from the elements of the groups 4A, 5A, 6A, 7A and 8 whose oxides exhibit n-type characteristics, wherein x, y and z are larger than 0 and smaller than 1 and 0.001 ≤ x/(1-y-z) < 0.20, 0.05 ≤ y/(1-y-z) ≤ 0.80 and 0 < z/(1-y-z) ≤ 0.90. Thermistor elements (1) made from the above ceramic composition are usable within a broad temperature range of 300-1100°C have a stable resistance in oxidizing and reducing atmospheres, can prevent deterioration of lead wires, and have superior stability at high temperatures.
- 🔍 Attorney, Agent or Firm: **DIEHL GLAESER HILT & PARTNER ;**
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⌚ Designated DE FR

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⌚ Family: [Show known family members](#) (at least 8)

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+ [Process Aspects](#)

+ [Process Aspects](#)

+ [Other Features of the Products](#)

+ [Other Features of the Products](#)

+ [Explanation of Symbols](#)

+ [Explanation of Symbols](#)

+ [EXAMPLES](#)

+ [EXAMPLES](#)

+ [Example 1](#)

+ [Example 1](#)

+ [EXAMPLE 2](#)

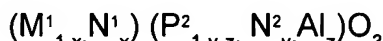
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⌚ First Claim: 1. A ceramic composition represented by the formula

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where M¹ is one or more elements selected from the group of the elements belonging to the group 3A of the Periodic Table excluding La, N¹ is one or more elements selected from the group of the elements belonging to the group 2A of the Periodic Table, excluding Mg, P² is one or more elements selected from the group of the elements Cr, Mn, Co and Ni, and N² is one or more elements selected from the group of the elements Fe, V, and Ti, wherein x, y and z are larger than 0 and smaller than 1 and satisfy the following formulas

$$0.001 \leq x/(1-y-z) < 0.20$$

$$0.05 \leq y/(1-y-z) \leq 0.80$$

$$0 < z/(1-y-z) \leq 0.90.$$

[\[German\]](#) [\[French\]](#)

⌚ Other Abstract Info: CHEMABS 122(10)120760G DERABS C1995-000868



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(54) **Ceramic composition, thermistor element, and process for producing a ceramic body**

Keramische Zusammensetzung, Thermistor Teil daraus und Verfahren zur Herstellung eines
keramischen Körpers

Composition céramique, élément thermistor et procédé pour la fabrication d'un corps céramique

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(56) References cited:
FR-A- 2 315 151 **US-A- 4 229 322**
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EP 0 626 356 B1

Description

[0001] The present invention relates to a ceramic composition, a thermistor element and a process for producing a ceramic body.

[0002] As materials for thermistors which may be employed at higher temperatures, there have so far been employed (a) a material composed mainly of compounds of a corundum type crystal structure, as disclosed for example in JP Patent KOKAI Publication No. 50-118294 (JP-A-118294/75) or "Fine Ceramics Handbook" by Kenya HAMANO, published by ASAKURA SHOTEN in 1984, (b) a material composed mainly of compounds of a spinel type crystal structure, as disclosed for example in JP Patent KOKAI Publication No. 49-63995 (JP-A-63995/74), (c) a material composed mainly of ZrO_2 , as disclosed in "Internal Combustion Engine" vol. 30, number 8, page 98, and (d) a material mainly composed of compounds of a perovskite type crystal structure. In JP-A-5 009 057 a perovskite structured complex oxide for electrodes is disclosed, said oxide containing rare earth metal e.g. lanthanum, alkaline earth metal e.g. calcium, and transition metal e.g. aluminium.

[0003] However, with the material (a) composed mainly of the corundum type crystal structure, it is not possible to adjust its resistance-temperature characteristics to a greater extent, although such characteristics can be changed slightly by addition of other elements. On the other hand, the material ceases to have a stable corundum structure and is deteriorated in thermal stability on addition of an additive in a larger quantity.

[0004] The material (b) composed mainly of compounds having the spinel type crystal structure has a higher rate of change of temperature-resistance characteristics, that is a temperature gradient constant β , such that it cannot be used over a wider temperature range. On the other hand, a material composed mainly of $NiAl_2O_4$, as disclosed in JP Patent KOKAI Publication No. 49-29493 (1974) (JP-A-29493/74) or a material composed mainly of $CoAl_2O_4$, as disclosed in JP Patent KOKAI Publication No. 48-705 (JP-A-705/73), is low in thermal resistance and cannot be used at elevated temperatures.

[0005] The material (c) composed mainly of zirconia has its resistance increased for a temperature range lower than its activation temperature and cannot be practically employed.

[0006] With the material (d) composed mainly of compounds having the perovskite type crystal structure, if only a small quantity of oxides of La is left unreacted, such unreacted component is reacted with the moisture in atmosphere to yield labile $La(OH)_3$ leading to destruction of the element or to unstable resistance values.

[0007] It is therefore the object of the present invention to provide a ceramic composition especially useful as a thermistor base, and a method of producing same, which avoids the above mentioned drawbacks of known products. This object is solved by the ceramic composition according to independent claim 1, the thermistor element according to independent claim 8 and the process to produce a ceramic body according to independent claim 21. Further advantageous features, aspects and details of the invention are evident from the dependent claims, the description, the examples and the drawings. The claims are to be understood as a first non-limiting approach to define the invention in general terms.

[0008] It is an aspect of the present invention to provide a novel ceramic devoid of the above mentioned problems.

[0009] It is a specific aspect of the present invention to overcome at least one of those problems and to provide a ceramic composition or a ceramic for thermistor in which at least one, preferably all of the following characteristics are satisfied: Namely, a broad range of resistance values may be obtained by adjusting the composition of the material, lead wires may be prevented from being deteriorated by being sinterable at a temperature not higher than $1600^\circ C$, and it is free from hygroscopic components and deterioration in characteristics due to environmental humidity or thermal hysteresis and hence may be used over a wide range of temperatures from room temperature up to $1100^\circ C$.

[0010] It is a further aspect of the present invention to provide a novel thermistor element and a thermistor device using the same.

[0011] Still further aspects will become apparent in the entire disclosure and claims.

[0012] This invention specifically relates to a ceramic composition for a thermistor having a negative temperature coefficient and exhibiting high stability at elevated temperatures and a thermistor element prepared from the composition.

[0013] As a result of our eager investigations, the present inventors have arrived at a ceramic composition, especially useful for thermistors, to achieve the above object. Namely, there is provided a composition represented by the general formula $(M^{1-x} \cdot N^1_x)(P^{2-y-z} \cdot N^2_y \cdot Al_z)O_3$ wherein M^1 denotes one or more elements selected from the elements belonging to the group 3A of the Periodic Table excluding La,

N^1 denotes one or more elements selected from the elements belonging to the group 2A of the Periodic Table,

P^2 denotes one or more elements selected from the elements which belong to the groups 4A, 5A, 6A, 7A and 8 and the oxides of which exhibit p-type characteristics,

N^2 denotes one or more elements selected from the elements which belong to the groups 4A, 5A, 6A, 7A and 8 of the Periodic Table and the oxides of which exhibit n-type characteristics, and

wherein x, y and z are larger than 0 and smaller than 1, and x, y and z are defined to satisfy the following formula

EP 0 626 356 B1

$$0.001 \leq x/(1-y-z) < 0.20,$$

$$0.05 \leq y/(1-y-z) \leq 0.80 \text{ and}$$

$$0 < z / (1-y-z) \leq 0.90.$$

[0014] A thermistor element can be produced using the above-defined composition.

[0015] The groups 2A, 3A, 4A, 5A, 6A and 7A herein mean the groups 2A, 3A, 4A, 5A, 6A and 7A of the Periodic Table for elements as agreed upon by the Committee for Nomenclature for Inorganic Chemistry of the International Union of Pure and Applied Chemistry (IUPAC) of 1970.

[0016] It has now been found that a desirable ceramic composition especially for thermistors may be provided by a composition represented by the general formula $(M^1_{1-x} \cdot N^1_x)(P^2_{1-y-z} \cdot N^2_y \cdot Al_z)O_3$ wherein M^1 denotes one or more elements selected from the elements Y, Sm, Pr, Nd, Dy, Er, Gd and Yb, and N^1 denotes one or more elements selected from the elements Mg, Ca, Sr and Ba,

P^2 denotes one or more elements selected from the elements Cr, Mn, Co and Ni, and

N^2 denotes one or more elements selected from the elements Fe, V and Ti,

wherein x, y and z are larger than 0 and smaller than 1, and x, y and z are defined so that

$$0.001 \leq x/(1-y-z) < 0.20, 0.05 \leq y/(1-y-z) \leq 0.80 \text{ and } 0 < z / (1-y-z) \leq 0.90.$$

[0017] It has also been found that a desirable ceramic composition especially for thermistors may be provided by a composition represented by $(Y_{1-x} \cdot Sr_x)(Cr_{1-y-z} \cdot Fe_y \cdot Al_z)O_3$ wherein M^1 is yttrium, N^1 is strontium, P^2 is chromium and N^2 is iron, wherein x, y and z are larger than 0 and smaller than 1, and x, y and z are defined so that

$$0.001 \leq x/(1-y-z) < 0.20, 0.05 \leq y/(1-y-z) \leq 0.80, \text{ and } 0 < z / (1-y-z) \leq 0.90.$$

[0018] It has also been found that a desirable ceramic composition especially for thermistors may be provided by a composition represented by $(Gd_{1-x} \cdot Sr_x)(Cr_{1-y-z} \cdot Fe_y \cdot Al_z)O_3$, wherein M^1 is gadolinium, N^1 is strontium, P^2 is chromium, and N^2 is iron, and

wherein x, y and z are larger than 0 and smaller than 1, and x, y and z are defined so that

$$0.001 \leq x/(1-y-z) < 0.20, 0.05 \leq y/(1-y-z) \leq 0.80 \text{ and } 0 < z / (1-y-z) \leq 0.90.$$

[0019] It has also been found that a desirable ceramic composition especially for thermistors may be provided by a composition represented by $(Sm_{1-x} \cdot Sr_x)(Cr_{1-y-z} \cdot Fe_y \cdot Al_z)O_3$, wherein M^1 is samarium, N^1 is strontium, P^2 is chromium and N^2 is iron, with x, y and z being larger than 0 and smaller than 1, wherein x, y and z are defined so that

$$0.001 \leq x/(1-y-z) < 0.20, 0.05 \leq y/(1-y-z) \leq 0.80 \text{ and } 0 < z / (1-y-z) \leq 0.90.$$

[0020] If a sintering aid is added to the ceramic composition especially for thermistors for improving its sinterability, it can be sintered at lower temperatures to give high strength and superior thermal resistance. As the sintering aids, those capable of forming a liquid phase in the grain boundary to form a matrix for improving the sinterability of the ceramic may be employed. The sintering aid is preferably added in an amount of 0.5 to 10 wt% and, in particular, in an amount of 0.8 to 5 wt%, based on the weight of the ceramic composition for the thermistor.

[0021] The following functions and/or advantages are achieved by the present invention.

[0022] The material according to the present invention is of the perovskite structure and exchange may be made easily between atoms having ion radii close to each other, and thus the compositions resulting from such atom exchanges exist in a stable state. Therefore, it becomes possible to change and adjust the composition continuously over a wide range.

[0023] Also, since the composition is free from La, it is not affected by the environmental humidity and may remain stable at higher temperatures so that it may be employed over a wide temperature range from room temperature up to 1100 °C or higher. This is thought to be ascribable to the fact that the compound of the present invention remains stable at higher temperatures.

[0024] The p-type semiconductor has its resistance dependency on the oxygen partial pressure which is converse to that of the n-type semiconductor. That is, the lower the oxygen partial pressure, the higher and the lower become the resistance of the p-type semiconductor and the n-type semiconductor, respectively. The ceramic composition of the

present invention is a mixture of these two semiconductor materials, the characteristics of which with respect to the oxygen partial pressure cancel each other, so that stable characteristics are exhibited despite fluctuations in the oxygen partial pressure. On the other hand, lattice defects of thermally labile oxygen or metal ions are diminished so that resistance values are not changed and remain stable even after heat hysteresis.

[0025] Since the ceramic composition is produced by simple substitution solid solution, it can be sintered at a temperature not higher than 1600 °C without producing by-products, while lead wires may be prevented from being deteriorated. In addition, sintered thermistor elements may be used over a wide temperature range of from room temperature to 1100 °C or higher. Furthermore, since the resistance values can be changed within a wide range by adjusting the composition in a wide range, it offers an advantage such that the resistance value and the thermal gradient constant (referred to as "β" hereinbelow) can be freely selected.

Process Aspects

[0026] According to the process aspects of the present invention, the following points are further mentioned which serve to illustrate the invention in more detail.

[0027] The calcination aims at to achieve a homogeneous sintered ceramic body with extensively reduced fluctuation in reaction, i.e., without segregated distribution of the phases which constitute the microstructure of the ceramic. In this regard, the starting materials are, preferably, selected from certain salts of the relevant elements, e.g., nitrates, sulfates, chlorides etc which are heat-decomposable with ease and have high reactivity upon heating for calcination.

[0028] Applying the calcination, particularly followed by pulverization, the fluctuation in the ultimate sintered products is believed to be significantly and with greater ease reduced to a minimum, as compared to the case where a mixture of the starting materials would be directly press-molded and sintered.

[0029] Thus, the calcination is carried out preferably within an approximate range of 1200 to 1450°C, more preferably about 1400°C. Also calcination is conducted until reaching a state where there is a minimum amount of nonreacted residues (in other words, reaction products of perovskite type compounds are easy for pulverizing without having been sintered with high densification). In this regard, the calcination will be continued, preferably, for at least about one hour, more preferably about 2 hours.

[0030] As for the sintering aid, there are many alternatives besides silica and/or mullite, such as, those compounds of types of CaO-SiO₂, SrO-SiO₂, MgO-SiO₂, B₂O₃-SiO₂-Al₂O₃, B₂O₃-SiO₂ and the like.

[0031] The sintering is preferably conducted at a temperature ranging 1450-1600°C, more preferably 1450-1550°C. The atmosphere for the sintering is generally preferred to be the ambient air or a neutral atmosphere (not oxidizing nor reducing). However, this will depend on the materials selected. For example, if SiO₂ is used as a sintering aid, oxidation of Cr(3+) to Cr(6+), volatilization and (even slight) reaction of SiO₂ with the major ingredients might serve to improve sinterability.

[0032] The sintering is carried out, preferably, for about at least one hour, more preferably, for about 1-2 hours until a sufficient density is reached, e.g., a relative density of 90% or more, or preferably 95% or more of the theoretical.

Other Features of the Products

[0033] The resulting sintered products consists essentially of perovskite type compounds, while there are phase(s) resulting from the sintering aid, usually as a grain boundary (matrix) phase which surrounds grains of perovskite.

[0034] The stable resistance is aimed at a resistance change rate as calculated as temperature being within plus/minus 15°C after the durability test under high temperatures (e.g., at 350, 600°C, 900°C).

[0035] Within the generic compositional range, the following range is preferred, e.g., according to Example 1:

$$0.0015 \leq x(1-y-z) \leq 0.020^*$$

$$0.05 \leq y/(1-y-z) \leq 0.80$$

$$0.20 \leq z/(1-y-z) \leq 0.90$$

[0036] The following meritorious effects are achieved by the present invention.

[0037] According to the present invention there are provided thermistor elements which can be used within a broad temperature range from 300°C to 1100°C and possess a stable resistance against both the oxidizing and reducing atmospheres. Also there are provided ceramic compositions for thermistors and thermistor elements which are superior in the stability at a high temperature, can be used within a broad temperature range, and have a high mechanical

* corresponds to the temperature gradient constant value "β" of 3000 or more.

strength, and thus they can be used as, for instance, a detecting device of overheating for the catalysts for exhaust gas purification in automobiles, measuring apparatus of high temperature gases such as detecting apparatus of the recycled gas temperature in the gas-recycling system of exhaust gas, measuring apparatus used at places of severe vibrations, or temperature measuring apparatus for various kinds of furnaces etc.

Figure 1 shows an embodiment of the present invention.

Explanation of Symbols

[0038]

- 1 thermistor element
- 2 lead wire

EXAMPLES

[0039] In the following preferred embodiments are disclosed with reference to specific Examples which should not be interpreted as limiting the invention thereto.

Example 1

[0040] Example 1 of the present invention is now explained.

[0041] Y_2O_3 having a purity of 99.9% or higher and a mean particle size of $1 \mu m$, $SrCO_3$ having a purity of 98.5% or higher and a mean particle size of $1 \mu m$, FeO_3 having a purity of 98.5% or higher and a mean particle size of $1 \mu m$, and Al_2O_3 having a purity of 99.9% or higher and a mean particle size of $0.7 \mu m$ were weighed to a composition $(Y_{1-x} \cdot Sr_x)(Cr_{1-y-z} \cdot Fe_y Al_z)O_3$ where x, y and z are set as shown in Table 1, mixed by a wet mixing method, dried and calcined (pre-fired) by subsequently maintaining the mixture $1400^\circ C$ for two hours.

[0042] To the resulting calcined powders 1 wt% of SiO_2 powder having a mean particle size of $0.8 \mu m$ is added and mixed by a wet mixing method. The resulting mass is mixed together by a wet method to give a slurry mixture which is then passed through a 200-mesh sieve and subsequently dried. The dried mass is then admixed with a binder composed of 15 wt% of poly vinyl butyral PVB, 10 wt% of di-butyl phthalate DBP, 50 wt% of methyl ethyl ketone MEK and 25 wt% of toluene for granulating powders for press molding.

Table 1

Sample No.	composition			resistance(k Ω)			β	
	x/1-y-z	z/1-y-z	y/1-y-z	350°C	600°C	900°C	300-600	600-900
1	0.000	0.20	0.20	135	2.08	0.107	9060	10100
2	0.000	0.80	0.20	173	6.64	0.496	7400	8860
3	0.0015	0.20	0.05	20.0	0.920	0.120	6700	7000
4	0.0015	0.20	0.10	19.0	0.960	0.108	6500	7460
5	0.0015	0.20	0.20	22.6	1.000	0.084	6680	8490
6	0.0015	0.20	0.25	26.7	1.06	0.089	6770	8450
7	0.0015	0.20	0.30	21.5	0.956	0.094	6840	7930
8	0.0015	0.20	0.50	15.0	0.820	0.091	6320	7500
9	0.0015	0.20	0.80	8.0	0.550	0.080	5800	6500
10	0.0015	0.30	0.20	67.7	1.84	0.121	7600	9280
11	0.0015	0.30	0.25	62.6	1.69	0.120	7720	9020
12	0.0015	0.30	0.30	50.8	1.55	0.125	7410	8580
13	0.0015	0.40	0.20	141	2.03	0.130	8880	9340
14	0.0015	0.40	0.25	107	1.51	0.111	9040	8900

EP 0 626 356 B1

Table 1 (continued)

Sample No.	composition			resistance(k Ω)			β	
	x/1-y-z	z/1-y-z	y/1-y-z	350°C	600°C	900°C	300-600	600-900
15	0.0015	0.40	0.30	42.3	0.874	0.091	8160	7700
16	0.0015	0.55	0.20	9.66	1.03	0.144	4680	6700
17	0.0015	0.55	0.25	31.6	2.20	0.196	5800	8220
18	0.0015	0.55	0.30	18.1	0.910	0.108	6500	7300
19	0.0015	0.80	0.20	31.1	2.50	0.327	5320	6890
20	0.0015	0.90	0.20	51.2	4.12	0.421	5480	7790
21	0.0020	0.80	0.20	6.24	1.26	0.259	3300	5400
22	0.0150	0.20	0.20	0.298	0.137	0.058	1870	3080
23	0.0200	0.80	0.20	0.394	0.174	0.086	1830	2380
24	0.200	0.80	0.20	0.122	0.032	0.014	990	2800
25	0.250	0.20	0.20	0.010	0.006	0.005	1260	610

[0043] The resulting powders are charged into a metal mold in which two platinum wires are disposed, each 0.4 mm in diameter, at an interval of 1.2 mm, and are pressed under a pressure of 98 MPa (1000 kg/cm²), for producing a molded product, 3 mm in diameter and 2 mm in thickness, having two lead lines of platinum wires, as shown in Fig. 1.

The molded products are sintered in ambient air at 1550°C to produce thermistor elements.

[0044] On the thermistor element, thus produced, resistance values in the atmosphere at 300°C, 350°C, 600°C and 900°C and values of the temperature gradient constant β were measured. The results are shown in the columns of the "resistance" and " β " in Table 1.

[0045] Next, the samples were maintained for 300 hours in the atmosphere at 1000°C and the resistance values thereof at 350°C, 600°C and 900°C before and after the maintenance at 1000°C were measured in order to check the durability by investigating the resistance change rate (referred to as " ΔR rate" hereinafter). The results are shown at the " ΔR rate (%)" column in Table 2. Also, environmental test was conducted by maintaining each sample at 900°C in a chamber of a reduced oxygen pressure at an oxygen partial pressure of 0.01 Pa (10⁻⁷ atm) followed by measuring the resistance values thereby checking the stability of the resistance values. The results are also shown at the column of "environmental test ΔR rate (%)".

Table 2

Sample No.	ΔR rate (%)			environmental test ΔR rate (%)
	350°C	600°C	900°C	
1	-30[10]	-18[15]	-10[12]	12[-15]
2	22[-13]	-11[10]	- 7[12]	16[-16]
3	17[- 9]	9[-10]	6[-12]	4[- 8]
4	9[- 5]	11[-12]	9[-15]	4[- 7]
5	6[- 4]	8[- 8]	5[- 8]	2[- 3]
6	- 4[3]	- 6[6]	- 6[9]	2[- 3]
7	- 8[5]	- 9[10]	- 2[4]	- 2[4]
8	- 8[5]	- 7[9]	- 3[5]	- 3[5]
9	-10[7]	- 7[10]	- 5[10]	- 5[10]
10	12[- 5]	9[- 7]	8[-10]	2[- 2]
11	8[- 4]	15[-12]	9[-13]	- 2[3]

Table 2 (continued)

Sample No.	ΔR rate (%)			environmental test ΔR rate (%)
	350°C	600°C	900°C	
1 2	-14[7]	- 9[7]	- 6[9]	- 3[4]
1 3	10[- 3]	7[- 5]	9[-12]	3[- 4]
1 4	6[- 2]	1[- 1]	1[- 2]	- 2[4]
1 5	-20[8]	-11[9]	- 6[10]	- 1[2]
1 6	3[- 2]	3[- 4]	3[- 6]	- 1[2]
1 7	10[- 6]	2[- 2]	5[- 8]	3[- 5]
1 8	-10[6]	- 7[8]	- 3[5]	1[- 2]
1 9	10[- 6]	2[- 3]	4[- 8]	1[- 2]
2 0	11[- 9]	10[-13]	6[-11]	- 2[4]
2 1	4[- 5]	3[- 4]	5[-12]	3[- 7]
2 2	5[- 8]	2[- 9]	5[-15]	0[0]
2 3	5[-10]	3[-10]	3[-15]	2[-10]
2 4	- 8[10]	7[-16]	3[-15]	0[0]
2 5	-14[48]	- 4[39]	- 5[110]	0[0]

[0046] The temperature gradient constant β , the resistance change (ΔR) rate and the resistance change rate calculated as temperature (converted temperature value derived from the resistance change rate) are defined by the following equations:

$$\beta = \ln(R/R_0)/(1/K - 1/K_0)$$

$$\Delta R \text{ rate} = (R_t - R_0)/R_0 \times 100\%$$

(ΔR rate, calculated as temperature)

$$= \beta \times K_0 / (\ln(R_t/R_0) \times K_0 + \beta) - K_0$$

where \ln indicates common logarithm, and R and R_0 indicate resistance values at absolute temperatures K and K_0 , respectively in the atmosphere. "300-600" and "600 - 900" denote the temperature gradient constants β between 300°C and 600°C and between 600°C and 900°C, respectively.

[0047] For the durability test, R_t denotes the resistance values at a temperature t ($t=300^\circ\text{C}$ or 900°C) in the atmosphere after the durability test. For the environmental test, R_t denotes the resistance values at a temperature t ($t=900^\circ\text{C}$) in an oxygen-reduced chamber. ΔR rate calculated as temperature is shown in the square brackets $[\]$ at the column of "environmental test ΔR rate" in Table 2.

[0048] As apparent from Table 1, the resistance value can be adjusted easily by varying the mixing ratios of $x/(1-y-z)$, $y/(1-y-z)$ and $z/(1-y-z)$ in the composition represented by the formula $(Y_{1-x} \cdot Sr_x)(Cr_{1-y-x} \cdot Fe_y \cdot Al_z)O_3$.

[0049] It has turned out that the resistance and β can be increased by substituting Fe and Al for the Cr sites in the composition $(Y_{1-x} \cdot Sr_x)(Cr_{1-y-z} \cdot Fe_y \cdot Al_z)O_3$. Therefore, there can easily be provided thermistor elements having required resistance values and β 's. This reaction system is substitution solid solution offering no yield of by products, and thus the resistance value can be adjusted easily, which is drawn to the advantage. As shown by the durability test and the environmental test, the products exhibit very stable characteristics against the heat hysteresis and oxygen partial pressure in the ambient atmosphere.

[0050] The smaller the more preferable is the changing rates of resistance in the durability test and the environmental test. However, it is preferred to be within 15°C (plus/minus) for the ΔR rate, calculated as temperature, which corresponds to Sample Nos. 3 to 23 in Table 2.

[0051] The reason for the above is thought as follows. On the one hand, it is ascribable to the decrease in the amount

of unstable metal ion defects and oxygen ion defects against the heat hysteresis owing to mixing YCrO_3 as a p-type semiconductor and Fe_2O_3 as an n-type semiconductor. On the other hand, it is ascribable to the compensation or cancellation of the dependency on the oxygen partial pressure through mixing of the p-and and n-type semiconductors.

[0052] Increase in the stability of resistance is observed also by substituting Sr for Y. However, the Sr substitution should be done within an extent such that it can be practically used, i.e., within the range $0.1\% \leq x/(1-y-z) < 20\%$ because an excess Sr substitution causes remarkable lowering in the resistance and β resulting in a deteriorated temperature dependent accuracy.

[0053] Next, the resistance change rate (ΔR rate) was investigated by keeping samples Nos. 5, 11, 14 and 17 at 1100°C in the ambient air for 20 hours. The results are shown in Table 3, which demonstrates that the inventive products do not suffer significant change in the resistance even after exposure to a high temperature of 1100°C . Also, a thermistor element having a high strength and a reduced deterioration of lead wires can be obtained since the sintering temperature is 1550°C .

Table 3

Sample No.	ΔR rate (%)		
	350°C	600°C	900°C
5	6[- 4]	8[- 8]	6[- 9]
11	- 9[5]	- 2[2]	2[- 3]
14	- 2[1]	3[- 3]	5[- 7]
17	7[- 4]	2[- 2]	4[- 7]

EXAMPLE 2

[0054] The second example will now be explained. Thermistor elements are produced according to the raw materials and method of Example 1 except for the following points, namely Gd_2O_3 having a purity of 99.9% or higher and a mean particle size of $1\ \mu\text{m}$ is used instead of Y_2O_3 , and the raw materials are weighed and mixed so as to provide compositions of Sample Nos. 26 and 27 of Table 4 by setting x, y and z in the formula $(\text{Gd}_{1-x} \cdot \text{Sr}_x)(\text{Cr}_{1-y-z} \cdot \text{Fe}_y \cdot \text{Al}_z)\text{O}_3$. The temperature-resistance characteristics of the resulting thermistor elements are additionally shown at columns "resistance" and " β ".

Table 4

Sample No.	composition			resistance(k Ω)			β	
	$x/1-y-z$	$z/1-y-z$	$y/1-y-z$	350°C	600°C	900°C	300-600	600-900
26	0.0015	0.40	0.25	59.2	1.773	0.126	6410	7753
27	0.0015	0.40	0.25	17.8	0.670	0.092	5469	6770
28	0.0015	0.40	0.25	2.19	0.300	0.066	4402	5168

[0055] The durability test and the environmental test were carried out in the same manner as in Example 1, and the results are also shown in Table 5.

Table 5

Sample No.	ΔR rate (%)			environmental test ΔR rate (%)
	350°C	600°C	900°C	
26	6.1[- 3]	6.8[- 5]	1.7[- 3]	-2.8[5]
27	10.6[- 6]	8.3[- 7]	4.0[- 8]	-1.5[3]

Table 5 (continued)

Sample No.	ΔR rate (%)			environmental test ΔR rate (%)
	350°C	600°C	900°C	
2 8	10.0[- 7]	7.2[- 8]	3.1[- 8]	-1.1[3]

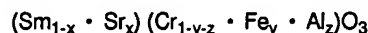
[0056] As apparent from Table 5, the resistance amounts to an order of 10 k Ω at 350°C and around 100 Ω at 900°C, respectively, which are suitable resistance values in the practice, while β assumes 5000 to 8000.

[0057] Accordingly, these samples are qualified as thermistor elements which are suitable for use in a temperature detecting apparatus, since they exhibit little change in the resistance value even after the durability test and the environmental test.

EXAMPLE 3

[0058] Next, the third Example will be explained.

[0059] Thermistor elements are produced according to the raw materials and method of Example 1 except for the following points, namely Sm₂O₃ having a purity of 99.9% or higher and a particle size of 1 μ m is used instead of Y₂O₃, and the raw materials are weighed and mixed so as to provide compositions of Sample No. 28 of Table 4 by setting x, y and z in the formula



[0060] The temperature-resistance characteristics of the resulting thermistor elements are additionally shown at columns "resistance" and " β ".

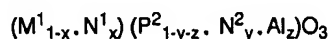
[0061] Also, the durability test and the environmental test were carried out in the same manner as Example 1 and the results are also shown in Table 5.

[0062] As apparent from Table 5, the samples are qualified as thermistor elements which are suitable for use in a temperature detecting apparatus, since they exhibit little change in the resistance value even after the durability test and the environmental test.

[0063] Samples Nos. 26 and 28 were subjected to a test at an extremely high temperature in which they were kept in the ambient air at 1100°C for 2 hours. The resulting resistance change rates exhibited within 10% at 350°C and within 5% at 900°C for each sample.

Claims

1. A ceramic composition represented by the formula



where M¹ is one or more elements selected from the group of the elements belonging to the group 3A of the Periodic Table excluding La, N¹ is one or more elements selected from the group of the elements belonging to the group 2A of the Periodic Table, excluding Mg, P² is one or more elements selected from the group of the elements Cr, Mn, Co and Ni, and N² is one or more elements selected from the group of the elements Fe, V, and Ti, wherein x, y and z are larger than 0 and smaller than 1 and satisfy the following formulas

$$0.001 \leq x/(1-y-z) < 0.20$$

$$0.05 \leq y/(1-y-z) \leq 0.80$$

$$0 < z/(1-y-z) \leq 0.90.$$

2. The ceramic composition as defined in claim 1

wherein M¹ is one or more elements selected from the group of Y, Sm, Pr, Nd, Ho, Dy, Er, Gd and Yb, and N¹ is one or more elements selected from the group of Ca, Sr and Ba.

3. The ceramic composition as defined in claim 2, wherein M¹ is Y, N¹ is Sr, P² is Cr and N² is Fe.

4. The ceramic composition as defined in claim 2, wherein M¹ is Gd, N¹ is Sr, P² is Cr and N² is Fe.
5. The ceramic composition as defined in claim 2 wherein M¹ is Sm, N¹ is Sr, P² is Cr, and N² is Fe.
- 5 6. The ceramic composition as defined in any one of claims 1 to 5 wherein the composition further comprises a sintering aid.
7. Use of the ceramic composition of one of the preceding claims for the production of a thermistor.
- 10 8. A thermistor element produced from the composition as defined in any one of claims 1 to 6.
9. The thermistor element produced from the composition as defined in claim 8 wherein the sintering aid is such that provides a liquid phase at grain boundary to form a matrix.
- 15 10. The thermistor element as defined in one of claims 8 or 9 wherein the sintering aid is present in an amount of 0.5 to 10 wt%, preferably 0.8 to 5 wt%.
11. The thermistor element as defined in one of claims 8 to 10 wherein the sintering aid is silica and/or mullite.
- 20 12. The thermistor element as defined in any one of claims 8 to 11 wherein the composition present is substantially of the perovskite structure.
13. The thermistor element as defined in one of claims 8 to 12 which has been produced by sintering said composition at a temperature not exceeding 1600°C.
- 25 14. The thermistor element as defined in one of claims 8 to 13 wherein said composition has been calcined at a temperature not exceeding about 1400°C, preferably at about 1400°C, before sintering.
15. The thermistor element as defined in one of claims 8 to 14 which has a resistance change rate, calculated as temperature, lying within +/-15°C.
- 30 16. The thermistor element as defined in one of claims 8 to 15 which has a temperature gradient constant β of 5000 to 8000.
- 35 17. The thermistor element as defined in one of claims 8 to 15 which has a temperature gradient constant β of at least 3000.
18. The thermistor element as defined in one of claims 8 to 17 wherein $0.0015 \leq x/(1-y-z) \leq 0.020$, and $0.20 \leq z/(1-y-z) \leq 0.90$.
- 40 19. The thermistor element as defined in any one of claims 8-18 wherein the composition has been calcined at 1200-1400°C.
20. The thermistor element as defined in one of claims 7 to 19 wherein the sintering aid is at least one selected from the group of silica, mullite, and materials of the types of CaO-SiO₂, SrO-SiO₂, MgO-SiO₂, B₂O₃-SiO₂-Al₂O₃ and B₂O₃-SiO₂.
- 45 21. The process for producing a sintered ceramic body comprising:
 - 50 (a) providing a ceramic composition represented by the formula (M¹_{1-x} · N¹_x) (P²_{1-y-z} · N²_y · Al_z)O₃ where M¹ is one or more elements selected from the group of the elements belonging to the group 3A of the Periodic Table excluding La, N¹ is one or more elements selected from the group of the elements belonging to the group 2A of the Periodic Table excluding Mg, P² is one or more elements selected from the group of the elements Cr, Mn, Co and Ni, and N² is one or more elements selected from the group of the elements Fe, V and Ti, wherein x, y and z are larger than 0 and smaller than 1 and satisfy the following formulas
 - 55

$$0.001 \leq x/(1-y-z) < 0.20$$

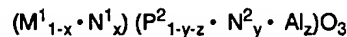
$$0.05 \leq y/(1-y-z) \leq 0.80$$

$$0 < z/(1-y-z) \leq 0.90, \text{ and}$$

- 5 b) sintering said composition, to a sintered body.
22. The process as defined in claim 21 wherein the composition further comprises an sintering aid.
23. The process as defined in claim 21 or 22 which further comprises a step of calcining a raw material mixture before
10 sintering.
24. The process as defined in claim 23 wherein the calcination is carried out about at 1200-1400°C, preferably about 1400°C.
- 15 25. The process as defined in claim 23 or 24 which further comprises, after the calcination, a step of pulverization before sintering.
26. The process as defined in any one of claims 21-25 wherein the sintering is carried out in a temperature range not exceeding 1600°C, preferably of 1450-1600°C, more preferably of 1450 to 1550°C.
- 20 27. The process as defined in claim 23 or 24 wherein the raw material mixture comprises at least one of salts of said elements.
28. The process as defined in one of claims 21 to 27, wherein the sintered ceramic body is a thermistor element.

25 **Patentansprüche**

1. Keramikzusammensetzung, dargestellt durch die Formel:



wobei M¹ für ein oder mehrere Elemente ausgewählt aus der Gruppe von Elementen der Gruppe 3A des Periodensystems ausschließlich La steht, N¹ für ein oder mehrere Elemente ausgewählt aus der Gruppe von Elementen der Gruppe 2A des Periodensystems ausschließlich Mg steht, P² für ein oder mehrere Elemente ausgewählt aus der Gruppe der Elemente Cr, Mn, Co und Ni steht und N² für ein oder mehrere Elemente ausgewählt aus der Gruppe der Elemente Fe, V und Ti steht,
35 wobei x, y und z größer als 0 und kleiner als 1 sind und folgende Formeln erfüllen:

$$0,001 \leq x/(1-y-z) < 0,20$$

$$0.05 \leq y/(1-y-z) \leq 0.80$$

$$0 < z/(1-y-z) \leq 0.90.$$

- 45 2. Keramikzusammensetzung gemäß Anspruch 1, bei der M¹ für ein oder mehrere Elemente ausgewählt aus der Gruppe von Y, Sm, Pr, Nd, Ho, Dy, Er, Gd und Yb steht, und N¹ für ein oder mehrere Elemente ausgewählt aus der Gruppe von Ca, Sr und Ba steht.
3. Keramikzusammensetzung gemäß Anspruch 2, bei der M¹ Y ist, N¹ Sr ist, P² Cr ist und N² Fe ist.
- 50 4. Keramikzusammensetzung gemäß Anspruch 2, bei der M¹ Gd ist, N¹ Sr ist, P² Cr ist und N² Fe ist.
5. Keramikzusammensetzung gemäß Anspruch 2, bei der M¹ Sm ist, N¹ Sr ist, P² Cr ist und N² Fe ist.
- 55 6. Keramikzusammensetzung gemäß einem der Ansprüche 1 bis 5, wobei die Zusammensetzung des weiteren eine Sinterhilfe umfaßt.
7. Verwendung der Keramikzusammensetzung gemäß einem der vorhergehenden Ansprüche für die Herstellung

eines Thermistors.

8. Thermistorelement, hergestellt aus der Zusammensetzung gemäß einem der Ansprüche 1 bis 6.

9. Thermistorelement, hergestellt aus der Zusammensetzung gemäß Anspruch 8, wobei die Sinterhilfe derart ist, daß eine Flüssigphase an der Korngrenze zur Bildung einer Matrix bereitgestellt ist.

10. Thermistorelement gemäß einem der Ansprüche 8 oder 9, bei dem die Sinterhilfe in einer Menge von 0,5 bis 10 Gew.%, vorzugsweise 0,8 bis 5 Gew.% vorliegt.

11. Thermistorelement gemäß einem der Ansprüche 8 bis 10, bei dem die Sinterhilfe Silika und/oder Mullit ist.

12. Thermistorelement gemäß einem der Ansprüche 8 bis 11, bei dem die vorliegende Zusammensetzung im wesentlichen von der Perowskitstruktur ist.

13. Thermistorelement gemäß einem der Ansprüche 8 bis 12, das durch Sintern der Zusammensetzung bei einer Temperatur von nicht mehr als 1600°C hergestellt wurde.

14. Thermistorelement gemäß einem der Ansprüche 8 bis 13, bei dem die Zusammensetzung bei einer Temperatur von nicht mehr als etwa 1400°C, vorzugsweise etwa 1400°C, vor dem Sintern kalziniert wurde.

15. Thermistorelement gemäß einem der Ansprüche 8 bis 14, das eine Widerstandsänderungsrate, als Temperatur berechnet, innerhalb von +/-15°C aufweist.

16. Thermistorelement gemäß einem der Ansprüche 8 bis 15, das eine Temperaturgradientenkonstante β von 5000 bis 8000 aufweist.

17. Thermistorelement gemäß einem der Ansprüche 8 bis 15, das eine Temperaturgradientenkonstante β von mindestens 3000 aufweist.

18. Thermistorelement gemäß einem der Ansprüche 8 bis 17, bei dem $0,0015 \leq x/(1-y-z) \leq 0,020$, und $0,20 \leq z/(1-y-z) \leq 0,90$ gilt.

19. Thermistorelement gemäß einem der Ansprüche 8 - 18, bei dem die Zusammensetzung bei 1200 - 1400°C kalziniert wurde.

20. Thermistorelement gemäß einem der Ansprüche 7 bis 19, bei dem die Sinterhilfe mindestens eine Sinterhilfe ausgewählt aus der Gruppe von Silika, Mullit und Materialien der Typen von CaO-SiO₂, SrO-SiO₂, MgO-SiO₂, B₂O₃-SiO₂-Al₂O₃ und B₂O₃-SiO₂ ist.

21. Verfahren zur Herstellung eines gesinterten Keramikkörpers, das folgendes umfaßt:

(a) Bereitstellung einer Keramikzusammensetzung, die durch die Formel $(M^{1}_{1-x} \cdot N^1_x)(P^2_{1-y-z} \cdot N^2_y \cdot Al_z)O_3$ dargestellt ist,

wobei M¹ für ein oder mehrere Elemente ausgewählt aus der Gruppe von Elementen der Gruppe 3A des Periodensystems ausschließlich La steht, N¹ für ein oder mehrere Elemente ausgewählt aus der Gruppe von Elementen der Gruppe 2A des Periodensystems ausschließlich Mg steht, P² für ein oder mehrere Elemente ausgewählt aus der Gruppe der Elemente Cr, Mn, Co und Ni steht und N² für ein oder mehrere Elemente ausgewählt aus der Gruppe der Elemente Fe, V und Ti steht,

wobei x, y und z größer als 0 und kleiner als 1 sind und folgende Formeln erfüllen:

$$0,001 \leq x/(1-y-z) < 0,20$$

$$0,05 \leq y/(1-y-z) \leq 0,80$$

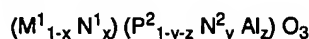
$$0 < z/(1-y-z) \leq 0,90, \text{ und}$$

(b) Sintern der Zusammensetzung zu einem gesinterten Körper.

22. Verfahren gemäß Anspruch 21, bei dem die Zusammensetzung des weiteren eine Sinterhilfe umfaßt.
23. Verfahren gemäß Anspruch 21 oder 22, das des weiteren einen Schritt der Kalzinierung einer Rohmaterialmischung vor dem Sintern umfaßt.
24. Verfahren gemäß Anspruch 23, bei dem die Kalzinierung in etwa bei 1200 - 1400°C, vorzugsweise etwa 1400°C erfolgt.
25. Verfahren gemäß Anspruch 23 oder 24, das des weiteren nach dem Kalzinieren einen Schritt der Pulverisierung vor dem Sintern umfaßt.
26. Verfahren gemäß einem der Ansprüche 21 - 25, bei dem das Sintern in einem Temperaturbereich von nicht über 1600°C, vorzugsweise von 1450-1600°C, noch bevorzugter von 1450 bis 1550°C, erfolgt.
27. Verfahren gemäß Anspruch 23 oder 24, bei dem die Rohmaterialmischung mindestens eines von Salzen der Elemente enthält.
28. Verfahren gemäß einem der Ansprüche 21 bis 27, bei dem der gesinterte Keramikkörper ein Thermistorelement ist.

Revendications

1. Composition céramique représentée par la formule



dans laquelle M¹ représente un ou plusieurs éléments choisis dans le groupe des éléments appartenant au groupe 3A de la Table Périodique à l'exclusion de La, N¹ représente un ou plusieurs éléments choisis dans le groupe des éléments appartenant au groupe 2A de la Table Périodique, à l'exclusion de Mg, P² représente un ou plusieurs éléments choisis dans le groupe des éléments Cr, Mn, Co et Ni, et N² représente un ou plusieurs éléments choisis dans le groupe des éléments Fe, V et Ti, x, y et z étant supérieurs à 0 et inférieurs à 1 et satisfaisant aux formules suivantes

$$0,001 \leq x / (1-y-z) < 0,20$$

$$0,05 \leq y / (1-y-z) \leq 0,80$$

$$0 < z / (1-y-z) \leq 0,90$$

2. Composition céramique selon la revendication 1, dans laquelle M¹ représente un ou plusieurs éléments choisis dans le groupe formé par Y, Sm, Pr, Nd, Ho, Dy, Er, Gd et Yb et N¹ représente un ou plusieurs éléments choisis dans le groupe formé par Ca, Sr et Ba.
3. Composition céramique selon la revendication 2, dans laquelle M¹ représente Y, N¹ représente Sr, P² représente Cr et N² représente Fe.
4. Composition céramique selon la revendication 2, dans laquelle M¹ représente Gd, N¹ représente Sr, P² représente Cr et N² représente Fe.
5. Composition céramique selon la revendication 2, dans laquelle M¹ représente Sm, N¹ représente Sr, P² représente Cr et N² représente Fe.
6. Composition céramique selon l'une quelconque des revendications 1 à 5, qui comprend en outre un auxiliaire de frittage.
7. Utilisation de la composition céramique selon l'une des revendications précédentes pour la production d'une thermistance.
8. Élément de thermistance produit à partir de la composition selon l'une quelconque des revendications 1 à 6.

9. Elément de thermistance produit à partir de la composition selon la revendication 8, dans lequel l'auxiliaire de frittage est tel qu'il donne une phase liquide à la limite des grains pour former une matrice.

10. Elément de thermistance selon l'une des revendications 8 ou 9, dans lequel l'auxiliaire de frittage est présent à raison de 0,5 à 10 % en poids, de préférence de 0,8 à 5 % en poids.

11. Elément de thermistance selon l'une des revendications 8 à 10, dans lequel l'auxiliaire de frittage est la silice et/ou la mullite.

12. Elément de thermistance selon l'une quelconque des revendications 8 à 11, dans lequel la composition présente a sensiblement la structure de la pérovskite.

13. Elément de thermistance selon l'une quelconque des revendications 8 à 12, qui a été produit par frittage de ladite composition à une température n'excédant pas 1600°C.

14. Elément de thermistance selon l'une quelconque des revendications 8 à 13, dans lequel ladite composition a été calcinée à une température n'excédant pas environ 1400°C, de préférence à environ 1400°C, avant le frittage.

15. Elément de thermistance selon l'une quelconque des revendications 8 à 14, qui a une vitesse de changement de résistance, exprimée en température, comprise entre +/-15°C.

16. Elément de thermistance selon l'une des revendications 8 à 15, qui a une constante de gradient de température β comprise entre 5000 et 8000.

17. Elément de thermistance selon l'une des revendications 8 à 15, qui a une constante de gradient de température β d'au moins 3000.

18. Elément de thermistance selon l'une des revendications 8 à 17, dans lequel $0,0015 \leq x/(1-y-z) \leq 0,020$, et $0,20 \leq z/(1-y-z) \leq 0,90$.

19. Elément de thermistance selon l'une quelconque des revendications 8 à 18, dans lequel la composition a été calcinée à 1200-1400°C.

20. Elément de thermistance selon l'une des revendications 7 à 19, dans lequel l'auxiliaire de frittage est un ou plusieurs des composés choisis dans le groupe comprenant la silice, la mullite et les matériaux du type CaO-SiO_2 , SrO-SiO_2 , MgO-SiO_2 , $\text{B}_2\text{O}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$ et $\text{B}_2\text{O}_3\text{-SiO}_2$.

21. Procédé de production d'un corps céramique fritté comprenant :

(a) la fourniture d'une composition céramique représentée par la formule $(\text{M}^1_{1-x} \text{N}^1_x) (\text{P}^2_{1-y-z} \text{N}^2_y \text{Al}_z) \text{O}_3$ dans laquelle M^1 représente un ou plusieurs éléments choisis dans le groupe des éléments appartenant au groupe 3A de la Table Périodique à l'exclusion de La, N^1 représente un ou plusieurs éléments choisis dans le groupe des éléments appartenant au groupe 2A de la Table Périodique, à l'exclusion de Mg, P^2 représente un ou plusieurs éléments choisis dans le groupe des éléments Cr, Mn, Co et Ni, et N^2 représente un ou plusieurs éléments choisis dans le groupe des éléments Fe, V et Ti, x, y et z étant supérieurs à 0 et inférieurs à 1 et satisfaisant aux formules suivantes

$$0,001 \leq x/(1-y-z) < 0,20$$

$$0,05 \leq y/(1-y-z) \leq 0,80$$

$$0 < z/(1-y-z) \leq 0,90 \text{ et}$$

(b) le frittage de ladite composition pour donner un corps fritté.

22. Procédé selon la revendication 21, dans lequel la composition renferme en outre un auxiliaire de frittage.

23. Procédé selon la revendication 21 ou 22, comprenant en outre une étape de calcination d'un mélange de matière

brute avant le frittage.

24. Procédé selon la revendication 23, dans lequel la calcination est mise en oeuvre à environ 1200-1400°C, de préférence à environ 1400°C.

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25. Procédé selon la revendication 23 ou 24, comprenant en outre, après la calcination, une étape de pulvérisation avant le frittage.

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26. Procédé selon l'une quelconque des revendications 21 à 25, dans lequel le frittage est mis en oeuvre dans une gamme de température n'excédant pas 1600°C, de préférence allant de 1450 à 1600°C, et mieux allant de 1450 à 1 550°C.

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27. Procédé selon la revendication 23 ou 24, dans lequel le mélange de matériau brut comprend au moins un sel desdits éléments.

28. Procédé selon l'une des revendications 21 à 27, dans lequel le corps céramique fritté est un élément de thermistance.

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FIG. 1

